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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
MASATO KOYAMA ET AL. : EXAMINER: HU, S.
SERIAL NO: 10/726,705 :
FILED: DECEMBER 4, 2003 : GROUP ART UNIT: 2811
FOR: A METHOD OF FORMING A :
SEMICONDUCTOR DEVICE
HAVING AN
AMORPHOUS/CRYSTALLINE
GATE INSULATING LAYER

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

I, Masato KOYAMA, a national of Japan, declare as follows:

I am a named inventor of the above-identified patent application.

I have reviewed the Official Action dated September 20, 2005, as well Takeshi et al. (Japanese Patent Application JP 2002-299607, herein "Takeshi") and it is my understanding the claims pending on September 20, 2005 were rejected as being unpatentable at least in part based on Takeshi's provision that nitrogen is formed in an insulating layer. In particular, it is my understanding that the rejection of the then pending claims was based on the finding that the insulating layer of Takeshi includes 10% or more nitrogen as disclosed in paragraph [0013] of Takeshi.

The following Experiments were conducted by me or under my direct supervision to show that a nitrogen concentration of 15 atom% or more in a surface region of the insulating

layer of Takeshi would not produce the 0.1 atom% concentration required by Takeshi in paragraph [0023].

In the method of Claim 18, an amorphous insulating layer containing nitrogen in a surface region thereof at a concentration of 15 atom% or more is formed on a substrate. Since the nitrogen concentration in the surface region of the amorphous insulating layer is 15 atom% or more, in the method of Claim 18, a solid-phase growth selectively occurs in the substrate side remnant region of the amorphous insulating layer and not in the surface region. As a result, a layered structure is formed within the insulating layer, including an epitaxial crystalline insulating layer and a surface part of the amorphous insulating layer remaining on the epitaxial crystalline insulating layer.

If the nitrogen concentration in the surface region of the amorphous insulating layer is less than 15 atom%, such a layered structure cannot be formed.

EXPERIMENTS:

The following steps have been performed:

HfSiON films containing nitrogen at 13 atom% were formed on a Si substrate, and were thermally processed at 1000°C. The cross sections of the obtained HfSiON films were observed with a TEM. Reference FIG. A (enclosed herewith) shows the result of the TEM observation.

As shown in Reference FIG. A, there is a black contrast as indicated with a white arrow. The black contrast shows that HfO₂ crystallization occurs. In the case where the nitrogen concentration is 13 atom%, a layered structure including an epitaxial crystalline insulating layer and the amorphous insulating layer remaining on the epitaxial crystalline insulating layer is not formed because the nitrogen concentration of 13 atom% was not enough to prevent the amorphous layer from becoming crystalline.

For comparison, HfSiON films containing nitrogen at 18 atom% were formed on a Si substrate, and were thermally processed at 1000°C. The cross sections of the obtained HfSiON films were observed with a TEM. Reference FIG. B (enclosed herewith) shows the result of the TEM observation.

Reference FIG. B shows a layered structure including an epitaxial crystalline insulating layer and the amorphous insulating layer (with no black contrast) remaining on the epitaxial crystalline insulating layer.

From the experimental results obtained by changing the nitrogen concentration, it was confirmed that the lowest nitrogen concentration of HfSiON films which prevent crystallization in a 1000°C thermal process was 15 atom% as disclosed in the specification.

Thus, the nitrogen concentration in the surface region of the claimed amorphous insulating layer has to be 15 atom% or more or otherwise the claimed structure cannot be obtained.

In contrast, in Takeshi (Takeshi et al., JP 2002-299607), the surface region of an amorphous insulating layer cannot include nitrogen at 15 atom% or more as will be discussed next. In Takeshi, the nitrogen content in the region of the insulating layer near the interface with a silicon substrate needs to be less than 0.1 atom% (see paragraph [0023] of the English translation of Takeshi). If the nitrogen concentration in the surface region (i.e., the region away from the interface between the insulating layer and the silicon substrate) is 15 atom%, the nitrogen content near the interface with the silicon substrate cannot be less than 0.1 atom%. To maintain the nitrogen concentration on the substrate side to be less than 0.1 atom%, the nitrogen concentration in the surface region is restricted to less than 15 atom%.

In support of my above stated position, submitted herewith is Sekine et al., "Nitrogen Profile Control by Plasma Nitridation Technique for Poly-Si Gate HfSiON CMOSFET with Excellent Interface Property and Ultra-low Leakage Current" as evidence.

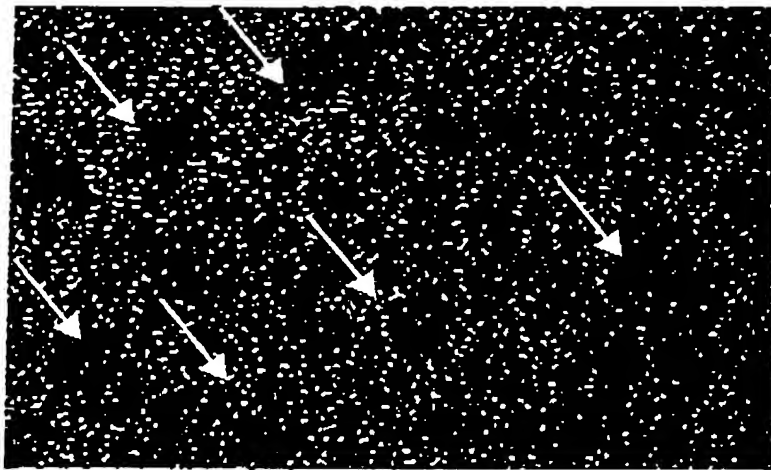
FIG. 10 of Sekine et al reference shows "nitrogen depth profiles measured by SIMS." FIG. 10(b) shows profiles obtained when nitrogen is doped by thermal nitriding. The thermal nitriding method is also used in Takeshi. As can be seen in FIG. 10(b), when the surface region of HfSiON films includes nitrogen at 15 atom%, the nitrogen concentration in the region of the insulating layer near the interface with the silicon substrate is about 1/10, not less than that. That is, in Takeshi, the nitrogen concentration in the surface region must not be 15 atom% or more so that the nitrogen concentration in the region near the interface with the silicon substrate is less than 0.1 atom%.

Thus, I believe that Takeshi does not teach or suggest the method of Claim 18.

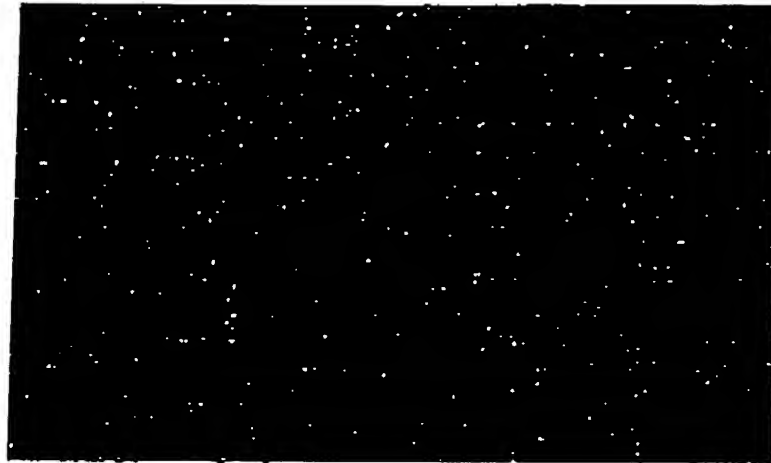
I, the undersigned, declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Date: Dec. 5, 2005

Masato Koyama
Masato KOYAMA



REFERENCE FIG.A



REFERENCE FIG.B

Nitrogen Profile Control by Plasma Nitridation Technique for Poly-Si Gate HfSiON CMOSFET with Excellent Interface Property and Ultra-low Leakage Current

Katsuyuki Sekine, Seiji Inumiya, Motoyuki Sato, Akio Kaneko, Kazuhiro Eguchi and Yoshitaka Tsunashima

Process & Manufacturing Engineering Center, Semiconductor Company, Toshiba Corporation
8, Shinsugita-cho, Isogo-ku, Yokohama, Kanagawa, 235-8522, Japan
Phone: +81-45-770-3668, Fax: +81-45-770-3577, E-mail: k-sekine@amc.toshiba.co.jp

Abstract

A comparative study of plasma and thermal nitridation of HfSiO was performed systematically. We found that over 15 atom% of nitrogen is necessary to obtain sufficient thermal stability and blocking of boron diffusion in conventional polycrystalline Si gate CMOS process regardless of the nitridation method. However, we demonstrated, for the first time, plasma nitridation has much advantage for obtaining thinner equivalent oxide thickness, lower gate leakage current ($J_g/J_{SiO_2} = 1E-4 @ V_g = V_{th} - 1V$) and higher carrier mobility ($\mu_{eff}/\mu_{SiO_2} = 0.85 @ E_{eff} = 0.8MV/cm$ for electron, $\mu_{eff}/\mu_{SiO_2} = 0.9 @ E_{eff} = 0.5MV/cm$ for hole) due to nitridation of HfSiO film without nitridation of Si substrate, compared with thermal nitridation.

Introduction

HfSiON film is considered to be a promising candidate for high-k gate dielectrics because of its good interface properties and sufficient thermal stability for integration with conventional polycrystalline Si (poly-Si) gate CMOS fabrication process [1]-[3]. Over the last few years, the effect of nitrogen in HfSiON has been the subject of controversy [1]. In our previous study, plasma nitridation (PN) [4][5] and thermal nitridation (TN) [6] were used for nitrogen incorporation in HfSiO films. However, it is not clear which nitridation method is preferable for obtaining better performance of CMOSFETs using HfSiON gate dielectrics with conventional poly-Si gate process. In this work, we investigated the difference between PN and TN as a nitridation method of HfSiO films in detail and demonstrated that PN enables us to obtain thinner equivalent oxide thickness (EOT), lower gate leakage current, and higher carrier mobility with high thermal stability while also preventing boron penetration to Si substrate.

Experimental

MOSFETs and MOS capacitors with HfSiON gate dielectrics were fabricated by conventional CMOS process with dopant activation annealing at 1000°C, 20sec as shown in Fig.1. HfSiON films were formed as follows. HfSiO films with Hf/(Hf+Si) ratio of 50% were directly deposited on hydrogen-terminated Si substrates by metal organic chemical vapor deposition (MOCVD). Post-deposition annealing (PDA) was carried out at 600-800°C in O₂ ambient for interface engineering. PN with Ar/N₂ mixed plasma at

R.T and TN in NH₃ ambient at 700-800°C were used for nitrogen incorporation in the HfSiO films. Post-nitridation annealing (PNA) was carried out at 800-1000°C in O₂ ambient. Nitrogen concentration in HfSiON films was measured by X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Fig.2 shows in-plane X-ray diffraction (XRD) spectra of both PN and TN nitrided HfSiON films with various nitrogen concentrations. Regardless of the nitridation method, HfSiON films with over 10 atom% nitrogen incorporation maintain amorphous state even after dopant activation annealing at 1000°C, 20sec.

Fig.3 shows backside secondary ion mass spectroscopy (SIMS) profiles of boron diffused from boron doped p⁺-poly-Si gate electrode to Si substrate after activation annealing at 1000°C. Resistance to boron penetration can be maintained by nitrogen incorporation of over 15 atom% for both PN and TN HfSiON.

The relationship between nitrogen content and flat-band voltage (V_{fb}) shift due to boron penetration is shown in Fig.4. The V_{fb} shift due to boron penetration was obtained by subtraction between V_{fb} of n⁺-poly-Si gate and p⁺-poly-Si gate MOS capacitor. The V_{fb} shift due to boron penetration becomes almost zero when over 15 atom% of nitrogen atoms are doped in the film. The results are consistent with the backside SIMS data shown in Fig.3. We revealed for the first time that sufficient thermal stability and resistance to boron penetration can be obtained by nitrogen incorporation of over 15 atom% regardless of the nitridation method.

Fig.5 shows Hf4f, Si2p and N1s XPS spectra of HfSiON after PNA. There is no significant difference in chemical bonding structure between PN and TN nitrided HfSiON. This is the main reason that thermal stability and boron blocking ability of both PN and TN HfSiON are almost same.

The main concern, when over 15 atom% of nitrogen atoms are doped in the film, is degradation of the interface properties. Fig.6 and Fig.7 demonstrate that carrier mobility of TN HfSiON degrades as nitrogen concentration increases, while the degradation of carrier mobility in both nMOS and pMOS can be suppressed by PN. This suppression is particularly marked in high nitrogen concentration region of over 15 atom%. High carrier mobility ($\mu_{eff}/\mu_{SiO_2} = 0.85 @ E_{eff} = 0.8MV/cm$ for electron and $\mu_{eff}/\mu_{SiO_2} = 0.9 @ E_{eff} = 0.5MV/cm$ for hole) can be obtained

while keeping sufficient thermal stability and resistance to boron penetration by PN.

Fig.8 and Fig.9 show V_{th} shift due to fixed charge and interface state density (D_{it}) of nMOSFET as functions of nitrogen concentration, respectively. The V_{th} shift and increase in D_{it} of PN HfSiON due to nitridation is smaller than those of TN HfSiON. The results indicate that generation of fixed charge and interface state due to nitrogen doped near HfSiON/Si substrate interface can be suppressed by PN. This is the main reason that PN can suppress degradation of carrier mobility even when over 15% of nitrogen atoms are doped in the film.

Fig.10 shows nitrogen depth profiles in PN and TN HfSiON measured by SIMS when nitrogen concentration in the film is varied. It is clearly demonstrated that nitrogen atoms are doped from the film surface by PN, whereas nitrogen atoms are doped not only in HfSiO film but in HfSiO/Si substrate interface by TN. These lower nitrogen concentration at HfSiO/Si interface realized by PN prevent generation of interface state and fixed charge, resulting in suppressing degradation of carrier mobility.

Fig.11 shows change of $Hf/(Hf+Si)$ ratio in HfSiON films when doped nitrogen concentration are varied. The behavior of physical thickness of HfSiON films with various nitrogen concentrations is shown in Fig.12. $Hf/(Hf+Si)$ ratio keeps constant and physical thickness slightly decreases as nitrogen concentration increases in PN HfSiON. On the other hand, $Hf/(Hf+Si)$ ratio decreases and physical thickness increases as nitrogen concentration increases in TN HfSiON.

A cross-sectional transmission electron microscopy (TEM) image of poly-Si/HfSiON/Si gate stack structure are shown in Fig.13. The results indicate that TN induces increase in physical thickness of interfacial layer by nitridation of Si substrate. The result is consistent with XPS and SIMS data shown in Fig.10-12. It is found that the decrease of $Hf/(Hf+Si)$ ratio and increase in physical thickness of the films by TN is caused by nitridation of Si substrate. The decrease in $Hf/(Hf+Si)$ ratio in TN HfSiON induces decrease of effective dielectric constant of the film.

Furthermore, the difference of nitridation mechanism between TN and PN strongly affects EOT and gate leakage current of HfSiON films. Fig.14 shows EOT of PN and TN HfSiON films as a function of nitrogen concentration. EOT reduction of PN HfSiON is larger than that of TN HfSiON at the same nitrogen concentration in the films.

Fig.15 shows the relationship between leakage current reduction (J_g/J_{gSiO_2}) and nitrogen concentration. The leakage current reduction of PN HfSiON decreases as nitrogen concentration increases, whereas that of TN HfSiON increases as nitrogen concentration increases.

Fig.16 shows gate leakage current of nMOS capacitors with PN and TN HfSiON gate dielectrics measured at ($V_{th}-1$) as a function of EOT. The EOT- J_g relationship of nMOS capacitors with SiO_2 are also shown in Fig.16 as a reference. The gate leakage current of PN HfSiON is about one order of magnitude lower (about 4 orders of magnitude lower than

that of SiO_2) than that of TN HfSiON at the same EOT. It is clearly demonstrated that PN has much advantage for obtaining not only higher carrier mobility but also thinner EOT, lower gate leakage current. They are because the increase of physical thickness and decrease of effective dielectric constant of TN HfSiON hinder reduction of EOT and gate leakage current, while PN can suppress decrease in effective dielectric constant and increase in physical thickness of the films.

Conclusions

The difference between PN and TN HfSiON was clearly demonstrated for the first time. Generation of D_{it} and fixed charge, decrease in effective dielectric constant and increase in physical thickness of the films (They are caused by nitridation of Si substrate.) are prevented by controlling nitrogen profile using PN. Consequently, thinner EOT, lower gate leakage current and higher carrier mobility can be realized by PN while keeping sufficient thermal stability and resistance to boron penetration for integration with conventional poly-Si gate CMOS device fabrication.

Acknowledgments

The authors would like to thank Dr. Shreyas Kher and Mr. Hirofumi Matsuo of Applied Materials for fruitful discussion on deposition process of HfSiO films. They are also grateful to Ms. Mariko Takayanagi and Dr. Takeshi Watanabe of Toshiba Corporation for supporting this study.

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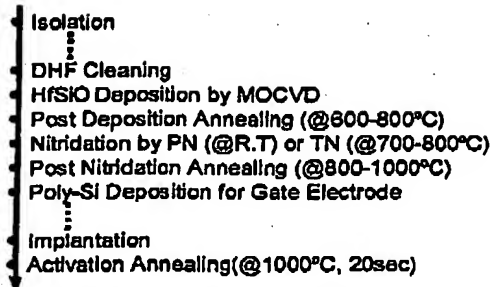


Fig.1 Fabrication process flow of MOSFETs and MOS capacitors with HfSiON gate dielectrics

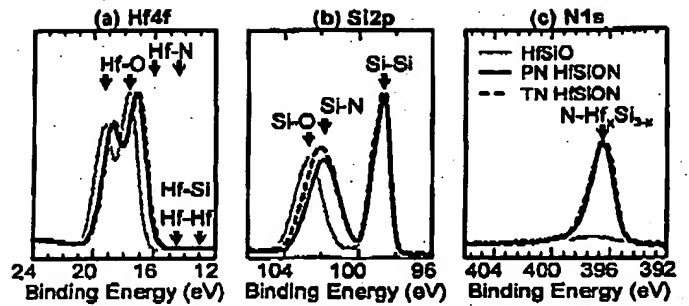


Fig.5 XPS spectra (Hf4f, Si2p, N1s) of TN and PN nitrided HfSiON with nitrogen concentration of 15atom%.

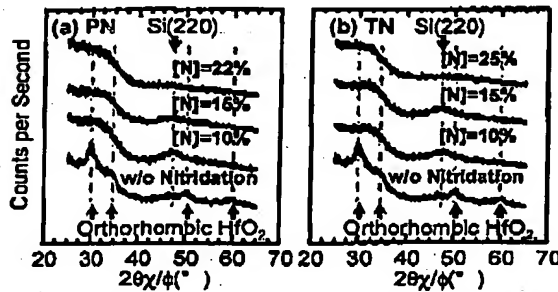


Fig.2 In-plane XRD spectra of (a) PN and (b) TN nitrided HfSiON after 1000°C 20sec annealing

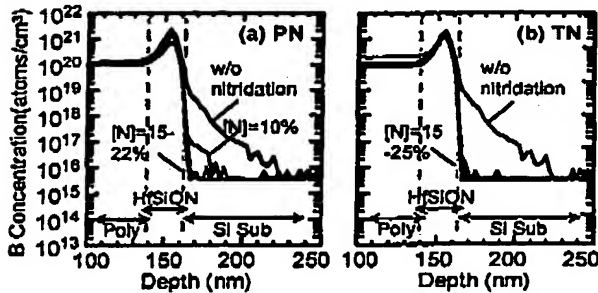


Fig.3 Depth profiles of boron diffused from boron doped poly-Si electrode to Si substrate ((a) PN and (b) TN)

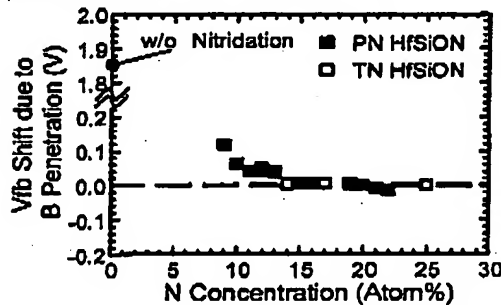


Fig.4 Vfb shift due to boron penetration as a function of nitrogen concentration

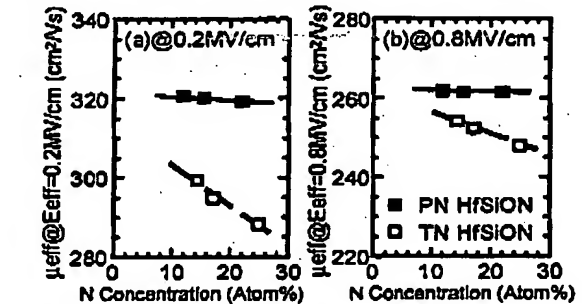


Fig.6 Electron mobility of PN and TN HfSiON vs nitrogen concentration ((a) @Eeff=0.2MV/cm, (b) @Eeff=0.8MV/cm)

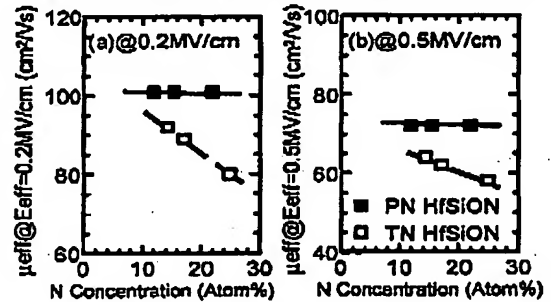


Fig.7 Hole mobility of PN and TN HfSiON vs nitrogen concentration ((a) @Eeff=0.2MV/cm, (b) @Eeff=0.5MV/cm)

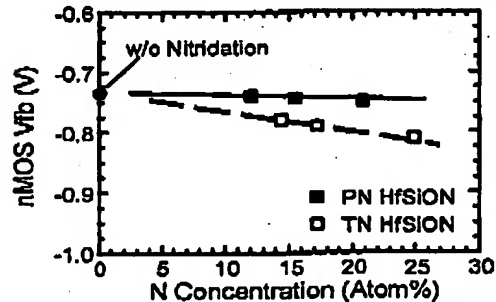


Fig.8 Vfb shift due to fixed charge of PN and TN HfSiON dependence on nitrogen concentration

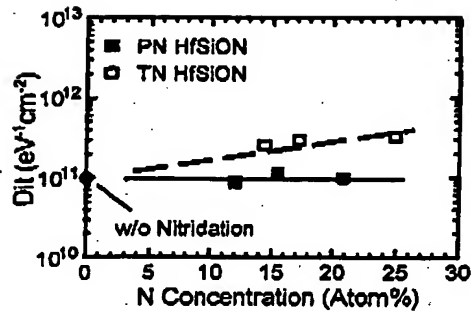


Fig.9 Dit of PN and TN HfSiON vs nitrogen concentration

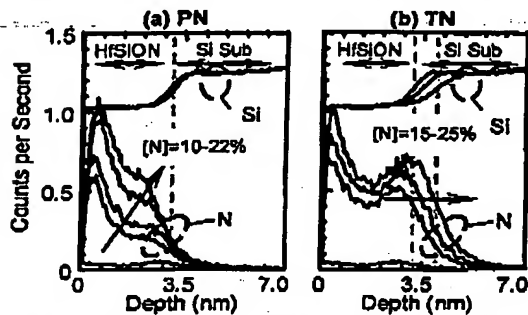


Fig.10 Nitrogen depth profiles in (a)PN and (b) TN HfSiON measured by SIMS

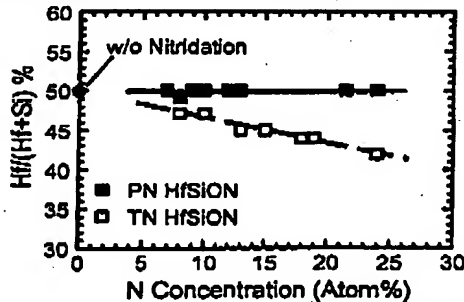


Fig.11 Relationship between Hf/(Hf+Si) ratio in HfSiON and doped nitrogen concentration

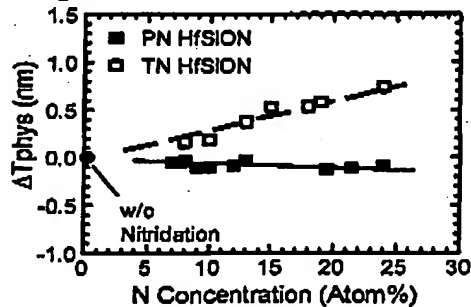


Fig.12 Behavior of physical thickness of HfSiON films on nitrogen concentration in HfSiON by PN and TN

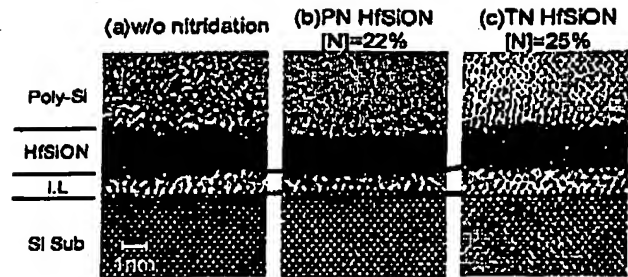


Fig.13 TEM images of Poly-Si/HfSiON/Si substrate structure, (a)w/o nitridation, (b)PN HfSiON, (c)TN HfSiON

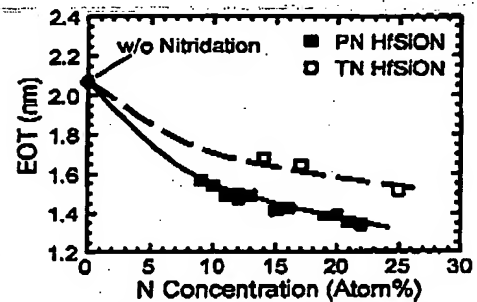


Fig.14 EOT of HfSiON nitrided by PN and TN as a function of nitrogen concentration

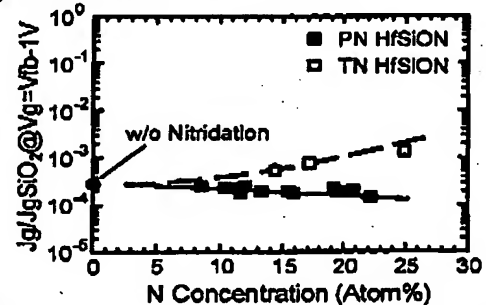


Fig.15 Gate leakage current reduction compared with the same EOT of SiO₂ (Jg/JgSiO₂) vs doped nitrogen concentration.

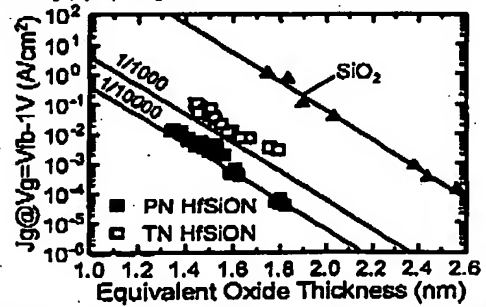


Fig.16 Summary of EOT-Jg relationship of HfSiON nitrided by PN and TN